Some Advances in Techniques for the Study of Adsorbed Monolayers at the Liquid-Air Interface

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VARIOUS devices for studying monolayers adsorbed at the interface between a liquid and air require the use of trays, sliding and floating barriers, and flexible connectors for the latter, all coated with a water-repellant material. The Langmuir film balance and its many modifications require that the parts be coated with paraffin wax or some other highly hydrophobic material to permit formation of a liquid level above the rim of the tray so that the surface of the water can be cleaned and the adsorbed film compressed by sliding barriers.[1] In many types of research with such equipment, metallic impurities in the water resulting from the use of metallic trays (even though waxed) make it impossible to use the latter, and waxed silica or Pyrex must be used. Metal trays coated with hydrophobic Bakelite lacquers have been used[2] but the protective film is not durable nor always impermeable. Furthermore, no satisfactory method of containing organic liquids at levels above the rim of the tray have appeared heretofore.

Polymers of tetrafluorethylene or "Teflon"[3] developed by the DuPont Company during the war are now commercially available. Many of the physical and chemical properties of Teflon have been described by Renfrew and Lewis.[4] Among the properties that make Teflon a nearly ideal material for making film balances are its chemical inertness, enabling the parts to be cleaned with solvents or by immersion in chromic-sulfuric acid; stability at high temperatures (250°C); hydrophobic and oleophobic surface properties; ease of working. A disadvantage is the difficulty in finding a cement for Teflon.

The difficulty in wetting Teflon surfaces is indicated by the following data on the contact angles of liquids on Teflon: water, 110°; glycerol, 105°; hexachlorobutadiene, 58°; di-(2-ethylhexyl) sebacate, 54°; dimethyltetraphenyldisiloxane, 54°; polymethylphenylsiloxane, 33°; cetane, 42°; polymethylsiloxane, 25°; isopropanol, 20°. The inability of many organic liquids to wet Teflon makes it possible to use trays of this material to contain organic liquids with the level of the liquid above the rim of the tray. This permits the use of techniques such as the sliding microtome of McBain[5] for measuring the concentrations of molecules adsorbed at the organic liquid-air interface. In the past this has been impossible.

Samples of Teflon obtained during the war were used by us in making accessories for film balances. Effective and durable flexible ribbons for connecting the floats to the sides of the tray were made by shaving 0.0005-inch thick ribbons from a small cube by means of a standard microtome. These ribbons were hydrophobic, unattacked by any of the solutions used, and were less likely to be damaged by accident than either platinum or silk. The lack of a suitable cement made it necessary to "rivet" the ribbons to the float and glass or metal tray by making a number of holes in the ribbons with a needle, and applying nitrocellulose cement so that the latter flowed through the holes to the surface beneath where it could attach itself.

Film balances entirely of Teflon were made for studying the force-area curves of substances adsorbed on the surface of organic liquids like mineral oil and hexachlorobutadiene. The tray contained these materials without leakage as long as the usual sliding barriers were not used. When the barriers were put in position, however, the liquid leaked because of capillarity at the area of contact of the barrier and the rim of the tray. This is to be expected with any liquid making a contact angle of less than 90°. Such difficulties can be avoided by the use of floating barriers sealed from end leakage by airjets in the manner used in Langmuir's original film balance.[1] The film pressures can advantageously be measured with a Wilhelmy balance.

Trays can be milled out of a single slab of Teflon while barriers and floats are easily made with ordinary shop equipment. Because of the softness of Teflon the usual polishing techniques cannot be employed to obtain smooth surfaces, but satisfactory surfaces can be generated by careful machining. Due to the tendency of Teflon to cold flow, it is advantageous to support large trays on a flat rigid plate which can be independently leveled. The use of cement is precluded in an all-Teflon tray, but when the tray is used with water, the parts may be riveted together.

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[2] J. W. McBain and R. F. Stuewer, Kolloid Zeits. **74**, 10 (1936).
[3] R. J. Plunkett, U. S., Feb. 4 (1941), pp. 2, 230, and 654.
[4] M. M. Renfrew and E. E. Lewis, Ind. Eng. Chem. **38**, 870 (1946).
[5] J. W. McBain and C. W. Humphreys, J. Phys. Chem. **36**, 300 (1932).

Small Cloud Chamber for Use with Unmanned Balloons*

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A SMALL, lightweight cloud chamber, designed for high altitude cosmic-ray researches, has been operated successfully in unmanned balloon flights up to an 80,000-ft. altitude.[1] In view of the current interest in high altitude cosmic-ray studies, it seems appropriate to describe briefly some of the design features of the present apparatus.

A radially expanding chamber four inches in inside diameter and two inches deep forms the nucleus of the apparatus. (See Fig. 1.) The radial expansion feature was chosen so that direct illumination could be used. A cylindrical rubber diaphragm (B), stretched between two circular glass end plates (F), forms the movable part of the chamber wall. The outward motion of this diaphragm is limited by a perforated cylindrical back-stop (A), and the chamber is compressed by admitting gas into the region behind the diaphragm. The expansion is initiated by tripping a solenoid-operated valve (C, D), which resets itself by spring action immediately after the expansion. The expansion ratio is determined by the pressure of the compressed gas behind the diaphragm. Needle valves (E) for filling the chamber are mounted in the glass plates.

The effects of changes in temperature are minimized by a specially constructed pressure regulator which serves both as a temperature compensation device and as a sensitive regulator to maintain the pressure within one or two millibars of the proper value for good tracks. (See Fig. 2.) The regulator contains a cavity (A) which can be filled with a gas and a small amount of some liquid. The output pressure of the regulator is determined by the pressure of the mixture inside this cavity and by the compression of an adjustable spring (B). The range over which the pressure can be adjusted by changing the spring compression is about fifty millibars. For a given spring force, the change in output pressure with a change in temperature is exactly equal to the change in pressure of the mixture inside the closed-off cavity. By selecting a liquid whose vapor-pressure curve has the proper slope, the regulator can be made to provide an output pressure which will maintain the proper expansion ratio for the cloud chamber. In practice, it was found that the cloud chamber mixture itself, in this case pure ethyl alcohol, is nearly a correct liquid to use. A 20 percent methyl–80 percent ethyl mixture gave good results from 18°C to 45°C. The lower limit is imposed by the small pressure differential between the cloud chamber and the atmosphere when the cloud chamber is in the expanded condition, and the upper limit by the difficulty of testing the chamber at elevated temperatures. It seems likely that such a system could be made to work satisfactorily over a considerably wider range. The temperature actually encountered in flight ranged from 10°C to 20°C; on a given flight it remained sensibly constant after the first thirty minutes of the flight. The temperature can be adjusted a few degrees by varying the relative amounts of light and dark material covering the apparatus.

The source of compressed gas is a small tank of liquid Freon suspended in the sunlight below the apparatus. The tank is painted black and is wrapped loosely with clear Cellophane. Freon gas is used in spite of its high specific gravity and molecular weight because it is non-corrosive, odorless, and non-inflammable. A slightly modified aircraft oxygen-flow pressure regulator is connected directly to the Freon tank and is adjusted to give an output absolute pressure of about 25 lbs. per square inch.

The effects of the changes in atmospheric pressure throughout the flight are minimized by enclosing the chamber and electrical system in a sheet aluminum sphere 12 inches in diameter. The absolute pressure inside this sphere is maintained at ground level atmospheric pressure by a sylphon-bellows pressure regulator located inside the sphere. The bellows unit is evacuated and sealed off, and has a strong spring inside it to keep it from collapsing. This unit was taken from one of the above aircraft oxygen-flow pressure regulators, specification No. AN6010-1.

Illumination is provided by a G.E. flash tube operated at 8 microfarads and 1100 volts. The tube is located perpendicular to the axis of the chamber, with either a plate in the chamber or a narrow baffle outside the chamber to prevent the camera from getting a direct view of the light. The increased intensity of the scattered light at low scattering angles is partially compensated by the penumbra of the shadow cast by the light baffle. The energy for the light flash is stored in five 40-microfarad electrolytic condensers connected in series. These condensers are charged by connecting a single 300-volt Minimax battery across each condenser in turn.

Photographs of the chamber are taken at 40-sec. intervals on 35-mm film by a twin-lens stereoscopic camera. The lenses are operated at $f/11$. The film is wound continuously, power being supplied by a small gas motor, operated by freon, located inside the sphere. This motor also provides the timing for the operating cycle and drives the switch which charges the condensers. The chamber is mounted with one glass end plate exposed to the outside of the sphere, and the camera is located outside the sphere. Photographs taken at high altitude indicate that thermal distortions (perhaps caused by a temperature difference across this plate and/or a temperature difference across the rubber diaphragm) are present, and would be serious if measurements were to be made of the curvature of the tracks in a magnetic field.

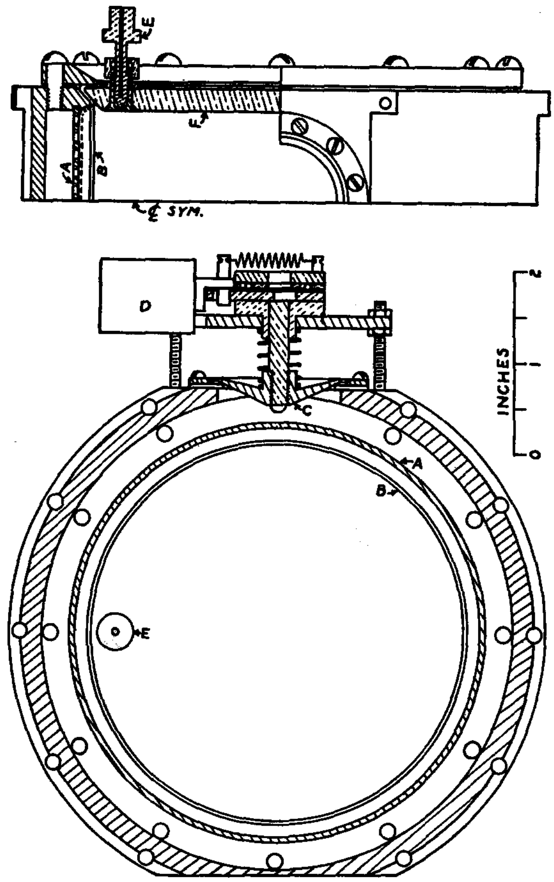

FIG. 1. Sectional drawing of radial cloud chamber showing main construction features.

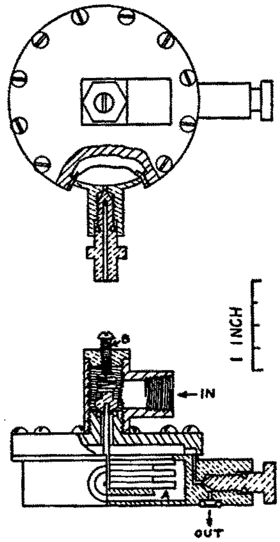

FIG. 2. Sectional drawing of temperature compensating pressure regulator used with radial cloud chamber.

An adjustable time delay between the discharge of the condenser which trips the chamber and the triggering of the light source is provided by an *R-C* network in the grid circuit of an OA5 trigger tube.

The main expansion in each cycle is followed after five or ten seconds by an underexpansion, which reduces the background fog and speeds up the recovery of the chamber after a possible overexpansion.

The entire apparatus is made light-tight so that the camera can be operated without lens shutters. A ½″ thick fiber glass blanket, one layer of black cloth, and a transparent Koroseal clothes bag cover the apparatus except the Freon tank, so that incident solar heat will be captured by the greenhouse effect.

FIG. 3. Typical cosmic-ray track photograph taken at 80,000 feet.

Temperature and altitude are measured by an alcohol-filled thermometer and a mercury manometer, placed in the field of view of the camera on either side of the chamber. The gross weight of the apparatus, ready for flight, is twenty pounds.

A typical photograph, taken at an 80,000-ft. altitude, is shown in Fig. 3.

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[1] See abstract No. F8, Bull. Am. Phys. Soc. 22, No. 5.

The Pumping Speed of an Oil Diffusion Pump for Hydrogen*

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IN many ion accelerators, the ion source supplies gas as well as ions into the vacuum system. Since in operation this gas is the major load on the vacuum pumps, it is important for design purposes to know the speed of the pumps for the gas used. It is planned to accelerate protons in the statitron at the University of Pennsylvania and, since it has been reported that the pumping of hydrogen presents anomalous features, a simple pumping speed measuring apparatus was set up.[1] Since hydrogen has a molecular weight of 2, it would be expected theoretically that its vacuum pumping properties would be $(29/2)^{\frac{1}{2}}$ or 3.8 times that of air.[1] The speed of the pump used was found to be roughly one-third as great for hydrogen as for air.

The pump was a four-inch, horizontal, self-fractionating, steel oil diffusion pump operated with silicone oil d.c. 702. At 325 watts' power input the manufacturers' data indicated a speed of 135 liters per second at a vacuum of 10^{-4} mm Hg (with octoil-S). At this power a pumping speed of 130 liters per second was measured for air but only 40 liters per second for hydrogen. The pressures were measured by an untrapped McLeod gauge and an ionization gauge calibrated for hydrogen and air separately against the McLeod. Parenthetically it may be noted that the silicone oil apparently poisons the oxide-coated filament of the ion gauge and requires more filament heating current to get the required emission. Since the manufacturers' data indicated that the pumping speed for air at 500 watts with octoil-S should be 240 liters per second, the pumping speeds were measured at the highest power we could obtain, 475 watts. The speeds increased, but in the same ratio, to 180 liters per second for air and 60 liters per second for hydrogen.

It has been suggested that the vapor stream in the pump may not be dense enough to prevent the light hydrogen gas from diffusing back though the pumping jet. Considerations of the heat conductivity, specific heat of the hydrogen, and